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# The thermal dissociation of $NH_2CHO$ ($ND_2CHO$) on Si(100)-2x1

by

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## Abstract

The interaction between $NH_2CHO(ND_2CHO)$ and Si(100)-2x1 has been investigated using HREELS, UPS and XPS. At 100 K, formamide molecules randomly adsorbed on the surface, but became ordered, likely with the O-atom attached to the surface, as the 2 L $NH_2CHO$ dosed Si(100) surface was warmed to 220 K. At this temperature, the formation of some Si-H species is indicated by the appearance of the 256 meV peak due to Si-H stretching vibration in HREELS. When the sample was annealed at 450 K, the OH and more H species were formed. In addition, a peak at 172(160) meV appeared in HREELS, which could be attributed to the HN=C (DN=C) and/or HNCO (DNCO) species. The latter species is more clearly evident in the UP spectrum. At 550 K, the breaking of CH, NH and probably some OH bonds continued and the OH and H dominated the adspecies. Further annealing the sample at higher temperatures caused the formation of Si-O-Si complex as indicated by the 129 meV peak in HREELS due to the asymmetric stretching mode of the Si-O-Si species. Above 800 K, the Si-H stretching mode at 260 meV decreased dramatically because of the desorption of the H-species.

## I. Introduction

The adsorption and thermal decomposition of $NH_2CHO$ on several metal surfaces have been investigated extensively[1-6], because formamide molecules may bond to the surface through N, C, O or the combinations of these atoms. Such studies are important for the understanding of the molecule-metal surface interaction in heterogeneous catalytic processes and will provide information for the comparison

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between the bonding and reactivity of various ligands in metal clusters and on metal surfaces.

On a Ru(001) surface, the CH bond breaking and the formation of a $\eta^2$(C,O)-$NH_2CO$ species occurred upon the adsorption of $NH_2CHO$ on the surface at $T_s \leq 225$ K.[1] Interestingly, when the Ru(001) surface was predosed with oxygen, $NH_2CHO$ bonded to the surface in an $\eta^1$(O)-$NH_2CHO$ geometry, which converted into $\eta^2$(N,O)-$NH_2CHO$ at 225 K.[2] On the other hand, on a hydrogen-presaturated Ru(001) surface, $\eta^1$(O)-$NH_2CHO$ species was found to convert into $\eta^2$(C,O)-$NH_2CHO$ at 225 K.[3] Thermal dissociation processes for $NH_2CHO$ on metal surfaces are also different. On Ru(001) (clean, H or O predosed), Rh(111) and Pt(111)[4] surfaces, $NH_2CHO$ dissociated into CO and $NH_x$ species through the breaking of the C-N bond. For formamide on Ni(111)[5], however, an additional reaction channel, i.e., $NH_2CHO \rightarrow HNCO(g) + H_2(g)$ was observed.

In searching for new N precursors for Si nitridation and CVD of group III-nitrides, we have recently studied the interaction of $NH_2CHO$ with an Si(100)-2x1 surface, because the $NH_x$ species could be effectively used as a nitrogen source if $NH_2CHO$ breaks into CO and $NH_x$ as observed on most of the metal surfaces. On the other hand, if $NH_2CHO$ dissociates into $CNH_x$ and $OH_x$ species through the cleavage of the C-O bond, the results could be compared with those obtained from the studies of other CN-containing molecules on Si substrates[7-9]. Such a study will provide useful information for the understanding of Si surface chemistry.

## II. Experimental

The experiment was carried out in a custom-designed UHV system (Leybold, Inc.) with a base pressure of $6 \times 10^{-11}$ torr as reported elsewhere[10,11]. X-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS) and

high resolution electron energy loss spectroscopy (HREELS) techniques were employed to characterize the surface species after an $NH_2CHO$ ($ND_2CHO$) dosed Si(100) surface was annealed at various temperatures. An Mg-source was utilized for XPS measurements and the electron energy analyzer was set at 50 eV to give an instrumental resolution of 1.3 eV. He(II) photon beam with an energy of 40.8 eV was used for UPS measurements. In HREELS, an electron beam with a primary energy of 5 eV and a full width at half maximum (FWHM) of 6 meV as measured in the straight-through mode was used.

A 2" diameter, B-doped Si(100) single crystal wafer from Virginia Semiconductor, Inc. was cut into 1.5 x 1.0 $cm^2$ samples. They were chemically cleaned with a hot HF solution and rinsed with deionized water. After being introduced into the UHV system, the Si samples were annealed repeatedly at $T_s \geq 1500$ K until no impurities, such as C, N and O, could be detected by AES, XPS and HREELS. $NH_2CHO$ (99%) and $ND_2CHO$ (99.6% pure and >99% D-enriched) from Aldrich and MSD isotopes, respectively, were purified by trap-to-trap distillation before use.

## III. Results

### a. *HREELS*

Figs. 1 and 2 present the HREELS results of $NH_2CHO$ and $ND_2CHO$ on Si(100)-2x1. When 2 L $NH_2CHO$ ($ND_2CHO$) was dosed on the surface at 100 K, the HREELS signals were weak and the elastic peak intensity was reduced by about 100 times as compared to that measured from a clean surface. Nevertheless, most of the molecular vibrational features were present in the HREEL spectrum. These observations suggest a random adsorption of formamide on the surface.

When the sample was warmed to 220 K, the elastic peak intensity was recovered and the HREELS signals became 20 times stronger. At this temperature, most of the molecular features were clearly present in the HREEL spectrum indicating no appreciable dissociation of the adsorbates.

The strong 27 meV peak due to the $NH_2$ torsional vibration became well resolved from the elastic peak. The intense peak at 87 meV has the contribution from the $NH_2$ wagging and OCN skeletal bending and possibly some from the Si-$OHCNH_2$ stretching vibration. The shoulder at ~135 meV is attributable to the $NH_2$ rocking and the CH bending modes, while the broad 175 meV peak is a mixture of the CH deformation and the C-N stretching vibrations. Other molecular vibrations are observed at 212, 363, 398 (305) and 413 (320) meV for the C=O, C-H, N-H (N-D) symmetric and N-H (N-D) asymmetric stretching modes, respectively. The $NH_2$ deformation mode expected at 199 meV is not resolved from the 212 meV peak; however, the relative intensity of the 135 meV peak is stronger in the $ND_2CHO$ spectrum due to the $ND_2$ deformation vibration. In addition, peaks at 230, 303 and a shoulder at 114 meV from the combinations of the fundamental modes also appeared in the $NH_2CHO$ spectrum. The vibrational frequencies for $NH_2CHO$ on Si(100) at various temperatures are listed in Table 1, while those for the gaseous and liquid $NH_2CHO$ and $NH_2CHO$ in $N_2$ matrix[12-15] and on metal surfaces are listed in Table 2 for comparison.

For $ND_2CHO$ (see Fig. 2), the 87 meV peak splits into two peaks, 75 and 110 meV. The former has contribution from the $ND_2$ wagging mode, while the latter is mainly due to the $ND_2$ rocking mode. The relative intensity change of the 135 peak upon the substitution of $NH_2$ with $ND_2$ is caused by the isotopic shift from 197 to 135 meV for the $NH_2$ ($ND_2$) deformation vibration. The $NH_2$ deformation mode was not clearly observed in the $NH_2CHO$ spectrum, because it is weak and obscured by its

adjacent intense peak at 212 meV. On the other hand, the weak $NH_2$ deformation mode may suggest one of the H atoms in $NH_2$ is bonded to the surface. In fact, some NH breaking was evident by the appearance of the 256 meV peak due to Si-H stretching vibration. In the $ND_2CHO$ experiment, the Si-D mode at 193 meV was not well resolved from its adjacent strong peaks at 175 and 212 meV.

After the surface was annealed at 450 K, the following changes were noticed because of the dissociation of the $NH_2CHO$ and the formation of new species on the surface. 1) The 256 and 193 meV peaks became stronger in the $NH_2CHO$ and $ND_2CHO$ spectra, respectively, indicating the further breaking of the NH (ND) bonds. The Si-H bending mode at 80 meV was also clearly evident in the spectra. These two peaks are consistent with those at 78 and 260 meV observed for monohydride on Si(100)-2x1[16]. 2) The disappearance of the CH stretching mode at 360 meV and the appearance of the OH stretching mode at 453 meV for both $NH_2CHO$ and $ND_2CHO$ indicate an H-transfer from the C to the O atom. The 453 meV peak is actually better resolved in the case of $ND_2CHO$, because there is less interference from the NH stretching mode (the NH bond may be formed by the H-D exchange in the system). This observation again suggests that the H-atom is transferred from the C, rather than the N atom to the O atom. Meanwhile, an intense peak at 103 meV due to the Si-OH bending vibration appeared, suggesting that the OH group is attached to the surface. An intense peak at 102 meV and a peak at 459 meV were observed when $H_2O$ dissociatively adsorbed on Si(100)-2x1[17]. The overtone of the Si-OH bending mode was also observed for $H_2O$ on Si(100)-2x1 as well as in the present study. 3) The formation of the OH radical implies that the other product would be $H_xNC$ species, which could be related to the new peak at 172 meV peak due to the HN=C stretching vibration in the $NH_2CHO$ spectrum. For $ND_2CHO$, this mode appeared at 160 meV as expected for the isotopic shift and its peak intensity was weak. This HN=C species is

similar to that of HN=CH formed in the thermal dissociation process of HCN on Si(100)[7]. The N=C stretching mode was at 160 meV and 124 meV for HN=CH and DN=CD, respectively, and the 124 meV peak intensity was also weak. The observed isotopic shift was larger for HN=CH (DN=CD) than HN=C (DN=C), because the former species is doubly deuterated. 4) The strong 260 meV mode, especially that in the $ND_2CHO$ spectrum, and the formation of OH bond (453 meV peak) suggest that the 260 meV peak may have contribution from components other than Si-H species, e.g., C≡N containing or more likely HNCO (DNCO) species. The latter, which should show another peak at ~170 (160) meV for the HNCO (DNCO) symmetric stretching vibration as observed in the HREEL spectra[5,18], is more convincingly evident in the corresponding UPS measurements. Finally, the 206 meV peak may have some contribution from the possible C=N species in addition to the overtone of the Si-OH bending mode.

At 550 K, the desorption and the dissociation of the HN=C (DN=C) and HNCO (DNCO) species were indicated by the disappearance of the 172 (160) meV peak and the attenuation of the NH ( ND) stretching mode at 423 (337) meV. Further annealing the sample at 700 K caused the formation of the Si-O-Si complex as indicated by the peaks at 50, 100 and 129 meV attributable to the rocking, symmetric and asymmetric stretching vibrations, respectively[16,19]. While the bending and stretching modes for the Si-H (Si-D) and species were at 78 and 262 (193) meV, respectively. The 78 and 100 meV peaks may have some contributions from the Si-C and Si-N stretching modes due to the survived C and N adspecies. Above 800 K, H species desorbed from the surface and some of the remaining H species bonded to the Si atoms which were back bonded to O atoms as indicated by the appearance of the hump at 280 meV.

b. *UPS*

When an Si(100)-2x1 surface was exposed to 2 L $NH_2CHO$ at 100 K, peaks at 5.0, 8.9, 11.0, 12.4 and 14.8 eV below $E_F$ were noted in the He(II) UP spectrum as shown in Fig. 3. By analogy to the gaseous $NH_2CHO$ UPS results[20,21], where peaks at 10.4 (10.7), 14.1 (14.8), 16.3, 18.8 and 20.7 eV were observed; these peaks could be assigned to the lone electron pairs in O and N, $\pi_{CO}$ and $\sigma_{CO}$, $\pi_{CN}$, $\pi_{NH2}$ and $C_{2S}$ molecular orbitals, respectively. The good agreement between the UPS results for the gaseous $NH_2CHO$ and $NH_2CHO$ adsorbed on Si(100) suggests that $NH_2CHO$ molecularly adsorbed on the surface. When this sample was warmed to 220 K, no significant changes were observed. However, the relative intensity of the $C_{2S}$ peak increased and that of the $\pi_{NH2}$ decreased slightly. These changes are likely due to the geometry change of the adsorbate and a slight dissociation of the NH bonds. On the other hand, the shift of all peaks toward lower binding energy by ~0.5 eV indicates a stronger interaction between adsorbate and substrate and a stronger screening effect on the final states.

When the sample was annealed at 450 K, a significant desorption of the adsorbate was indicated by the signal intensity decrease of about 80%. In addition, the $NH_2CHO$ molecular characteristic features disappeared and the spectrum was dominated by the peaks at 4.9 with a higher energy tail, 8.9 and 10.8 eV. This spectrum well resembles that of the gaseous HNCO[22], in which peaks were at 11.6, 12.4, 15.5 and 17.4 eV due to $\pi_{nb}$, $\pi_{nb}$, $\pi_b$ and N-H bonding orbitals, respectively. In the present study, the two $\pi$-nonbonding orbitals were not resolved, but a higher energy tail at 4.9 eV peak was evident. Other adspecies, such as OH and C=N containing species as identified by HREELS, also contribute to these peaks.

At 550 K, two new peaks at 6.7 and 11.2, similar to those reported for atomic O on Si(100), are mainly due to the OH species. On the other hand, the comparatively strong 11 eV peak observed here is because of the presence of the OH and a trace of NH species. These species decomposed when the surface was further annealed at higher temperatures, as indicated by the decrease of the 11 eV peak.

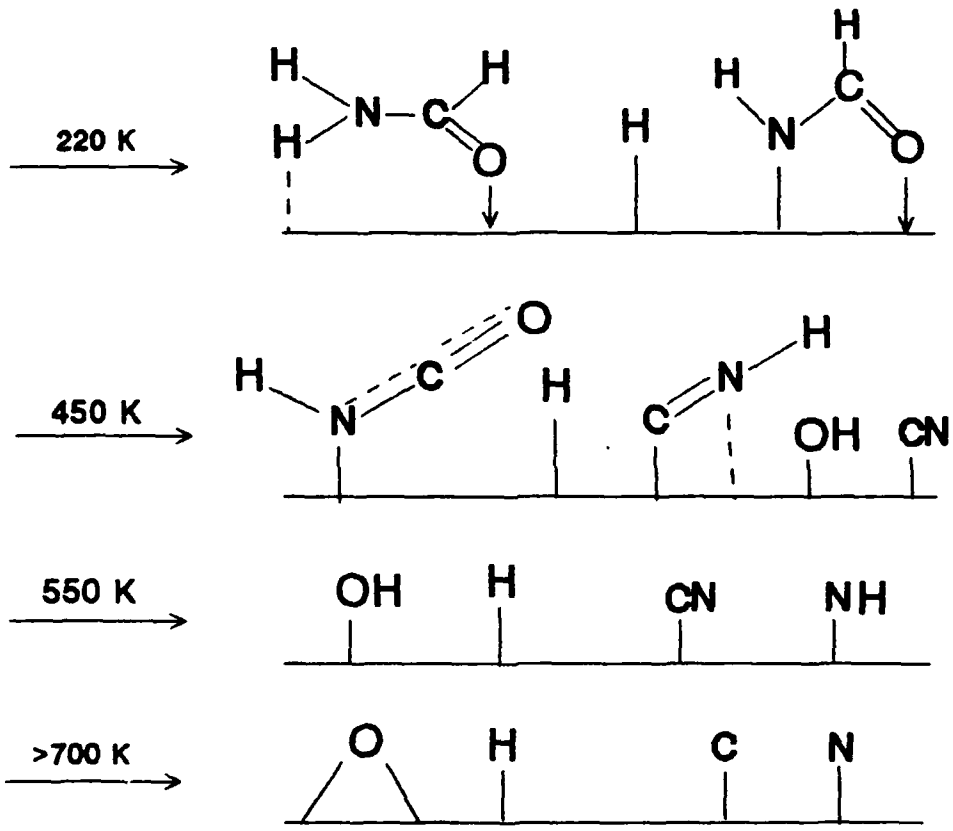
c. *XPS*

The thermal effects on the XPS results for $NH_2CHO$ on Si(100) are shown in Fig. 4. When 2 L $NH_2CHO$ was dosed on Si(100)-2x1 at 100 K, peaks were observed at 533.4, 400.9 and 289.9 eV with FWHM's of 2.2, 1.7 and 1.7 eV for $O_{1S}$, $N_{1S}$ and $C_{1S}$ photoelectrons, respectively. When the sample was warmed to 220 K, both $N_{1S}$ and $C_{1S}$ peaks shifted toward lower binding energy by 0.4 eV with no obvious peak intensity or peak width changes. In contrast, the $O_{1S}$ peak shifted toward lower binding energy by 1.1 eV with its peak intensity and FWHM reduced by 50% and 0.5 eV, respectively. These transformations obviously indicate a geometry change of the adsorbate, likely with the O-atom bonding to the surface at 220 K. The attenuation of the $O_{1S}$ XPS signal cannot be caused by the desorption of the possible CO or $H_2O$ adsorbed on the surface at 100 K, since there is no peak at ~260 (CO or Si-H stretching mode) or 460 (OH stretching mode) meV in the corresponding HREEL spectrum at 100 K. Annealing the surface at 450 K caused substantial desorption and dissociation of the adsorbates. The $O_{1S}$ peak continued to shift toward lower B.E. and its peak intensity further decreased by 70%. While the $N_{1S}$ and $C_{1S}$ photoelectron signals became too weak to give any conclusive information, because of the desorption of the adsorbates and the coexistence of the different C- and N-containing adspecies as identified by both HREELS and UPS measurements. Above 700 K, a single peak at 531.7 eV was observed for $O_{1S}$ photoelectron due to the formation of atomic O on the surface.

## Discussion

Based on HREELS, UPS and XPS measurements, the thermal decomposition of $NH_2CHO$ ($ND_2CHO$) on Si(100)-2x1 can be summarized as follows:

$$NH_2CHO(g) \xrightarrow{100K} NH_2CHO(a)$$




At 100 K, $NH_2CHO$ randomly adsorbed on the surface as indicated by the weak HREELS signals, especially the decrease of the elastic peak intensity by about 100 times as compared to that from the clean surface, and by the relatively broad $O_{1S}$ XPS peak.

After the sample was warmed to 220 K, the HREELS signal intensity was recovered, the relative intensity of the $C_{2S}$ peak in UPS increased and the $O_{1S}$ XPS peak intensity decreased. These changes suggest that $NH_2CHO$ molecules became ordered on the surface, presumably with the O lone-electron pairs attached to the surface and the C atom pointed away from the surface. Other supporting evidence for such an adsorption geometry is the larger energy shift of the $O_{1S}$ than the $N_{1S}$ and $C_{1S}$ XPS peaks and the decrease of the $O_{1S}$ XPS signal intensity, but not those of the $N_{1S}$ and $C_{1S}$ peaks. On the other hand, the observed Si-H (Si-D) stretching mode in HREELS, although weak, indicates a slight dissociation of the NH bond.

At 450 K, the XPS and UPS signals attenuated significantly due to the partial desorption of the adsorbates. At this temperature, the HREEL spectrum was dominated by the Si-H bending, Si-OH bending and Si-H stretching modes at 80, 103 and 256 meV, respectively. The corresponding OH stretching mode at 453 meV is not well resolved from those of the NH stretching vibration. However, it is clearly observed at 453 meV in the $ND_2CHO$ spectrum because of the smaller NH interference. All these peaks were observed in HREELS when $H_2O$ adsorbed on Si(100) at 300 K due to the partial dissociation of $H_2O$ into OH and H species[17]. Comparing these two HREELS results suggests that OH and H species also present on the surface after annealing the 2 L $NH_2CHO$ dosed Si(100) at 450 K. Since OH is formed on the surface, the other product would be expected as HN=C species, which can be related to the 172 (160) meV peaks to account for the HN=C (DN=C) stretching mode. Previously we have reported that after warming an HCN(DCN) dosed Si(100) surface to 220 K, the HN=CH (DN=CD) adspecies was formed[7]. The HN=CH (DN=CD) species showed a peak at 160 (124) meV for the N=C stretching mode and the observed large isotopic shift is due to the double deuteration of this species. The formation of the HN=C (DN=C) species in the present study is also supported by the

DN stretching mode at 337 meV, which is higher than the reported values for $ND_2CHO$ (317) or $DN_x$ (320) species on Si surfaces, but is close to the value observed for D-N≡C (342 meV) species. In the $NH_2CHO$ experiments, the H-NC stretching mode is not well separated from the OH stretching vibration mode.

Furthermore, the 260 meV peak is too strong to be attributed purely to the Si-H stretching mode, especially in the $ND_2CHO$ HREEL spectrum where the Si-H stretching peak is expected to be weaker. It is likely that the 260 meV peak has some contribution from another species, HNCO. The HNCO species was also formed on Ni(111), when an $NH_2CHO$ dosed Ni(111) surface was warmed to 285 K[5]. In this case, two peaks at 170 and 273 meV were observed in the reflection-adsorption IR spectrum. When adsorbed on Pt(111)[23], HNCO showed peaks at 169 and 282 meV for the two NCO stretching vibrations, while the two HNCO bending modes were at 66 and 108 meV. The latter two peaks could be obscured by the strong 80 and 103 meV peaks in the present study and the two NCO stretching modes can be correlated with the 172 and 260 meV peaks observed here. In the case of $ND_2CHO$, the DNCO symmetric stretching mode is shifted to 160 meV (see Fig. 2). The formation of the HNCO species is more convincingly evident in the correpsonding UPS results. At 450 K, all the $NH_2CHO$ molecular features disappeared, instead peaks at 4.9 with a shoulder at 5.6, 8.9 and 10.8 dominated the UP spectrum. These peaks compare favorably with those of gaseous HNCO UPS results, i.e., the peaks at 11.6, 12.4, 15.5 and 17.4 eV, if a value of 6.6 eV is taken for the surface work function and the relaxation of the adsorbates upon the adsorption on Si(100).

Apparently the OH and H species are the major adspecies as determined by HREELS, while the HNCO species seems to dominate the corresponding UP spectrum. We speculate that the HREELS technique is more sensitive to the OH and H species due to the dipole scattering, but HNCO species has bigger cross section in

the UPS measurement, because this species stretches out further away from the surface. Such a suggestion was made earlier by Schmeisser in the studies of $H_2O$ on Si(100)[24]. At 300 K, $H_2O$ molecular features (6.4, 7.4 and 11.8 eV peaks) dominated the UP spectrum, while OH (103 and 459 meV) and H (260 meV) species dominated the HREEL spectrum taken under similar experimental conditions.

At 550 K, the strong 4.9 eV peak disappeared and two peaks at 6.4 and 10.8 eV appeared in the UP spectrum. These two peaks are the characteristic features of atomic O on Si(100)[24,26], while the comparatively strong 10.8 eV peak is attributable to a partial contribution from the OH and a small amount of NH species. In addition, a weak feature at 4.4 eV may be attributed at least partially to the H-species. In the HREEL spectrum, the 172 (160) meV peak diminished, the relative intensity of the 260, 423 (337) and 453 meV peaks attenuated and the 210 meV peak became better resolved. The latter peak is likely due to the overtone of the 103 meV mode and to some extent the stretching vibration of the C=N species. The disappearance of the HNCO features in both UPS and HREELS and the decrease of the $O_{1S}$ XPS peak intensity at 550 K indicate the decomposition of HNCO and the desorption of HNCO or other O-containing species, e.g., CO species, which could be formed through the breaking of HN-CO bonds. It is worth mentioning that the 103 meV peak in HREELS should have some contribution from other components, such as Si-O, Si-N stretching and NH bending vibrations, since the 455 meV feature is rather weak at 550 K and the NH stretching mode is still present in the HREELS.

Further heating of the sample at 700 K caused the complete dissociation of the OH and NH bonds, as their stretching vibration peaks disappeared in the HREELS and the 10.8 eV peak attenuated and shifted toward lower binding energy in the corresponding UPS. Meanwhile, the formation of the Si-O-Si species is clearly indicated by the appearance of the 129 meV peak in HREELS due to the Si-O-Si

asymmetric stretching mode. Above 800 K, the desorption of the H species is evident by the virtual disappearance of the Si-H (Si-D) stretching mode.

## Conclusion

The thermal dissociation of $NH_2CHO$ ($ND_2CHO$) on Si(100)-2x1 has been investigated using HREELS, UPS and XPS. $NH_2CHO$ was found to randomly adsorb on Si(100) at 100 K and to become ordered, likely with the O-atom attached to the surface, when the sample was warmed to 220 K. When the surface was heated to 450 K, two reaction pathways were evident:

1) $NH_2CHO(a) \rightarrow OH(a) + HN{=}C(a) + H(a)$

2) $NH_2CHO(a) \rightarrow HNCO(a) + 2H(a)$.

Heating the surface at 550 K caused further desorption and dissociation of the adsorbates and OH and H species were identified as the major adspecies. Above 700 K, Si-O-Si complex was formed on the surface following the breaking of the OH bonds, while H species desorbed from the surface at $T_s \geq 800$.

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**Figure Captions:**

1. The thermal effect on the HREELS taken from a 2 L $NH_2CHO$ dosed Si(100)-2x1 sample. (For visual clarity, the figure has been broken into a and b).

2. The thermal effect on the HREELS taken from a 2 L $ND_2CHO$ dosed Si(100)-2x1 sample. (For visual clarity, the figure has been broken into a and b).

3. The thermal effect on the He(II) UP spectra for a 2 L $NH_2CHO$ dosed Si(100)-2x1 sample. All the curves are the differential spectra obtained by subtracting the spectra taken from the dosed and annealed samples from that taken from the clean surface.

4. The thermal effect on the XPS of a) $O_{1S}$, b) $N_{1S}$ and c) $C_{1S}$ photoelectron taken from a 2 L $NH_2CHO$ on Si(100)-2x1 sample; dosed at 100 K and then annealed at the indicated temperatures.

Table 1. The observed vibrational frequencies for $NH_2CHO(ND_2CHO)$ on Si(100)-2x1 at different temperatures.

| Mode | 100 K | | 220 K | | 450 K | | | 550 K | | | 700 K | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\nu_a$(NH) | 420 | (312) | 413 | (315) | $\nu$(OH) | 453 | (453) | 453 | (453) | | | |
| $\nu_s$(NH) | 400 | | 398 | (305) | | 425 | (337) | 430 | (3337) | | | |
| $\nu$(CH) | 363 | (363) | 363 | (362 | $\nu$(Si-H) | 260 | (193) | 260 | (193) | | 262 | (193) |
| $\nu$(CO) | 210 | (212) | 212 | (212) | $\nu_{a(HNCO)}$ | | (260) | | | | | |
| $\delta(NH_2)$ | | | | (135) | $2\beta$(Si-OH) | 206 | (210) | 210 | (210) | | | |
| $\delta$(CH) | 175* | (173) | 175* | 175* | $\nu_{s(HNCO)}$ | 172* | (160)* | | | | $\nu_{a(Si-O-Si)}$ | 129 (129) |
| $\nu$(CN) | | | | | $\nu$(HN-C) | | | | | | | |
| $\rho(NH_2)$ | 130* | (103) | 135* | (110) 135* | $\nu$(Si-O) $\beta$(Si-OH) | 103* | (105) | 103* | (104) | | $\nu_s$(Si-O) | 101 (101) |
| $\pi$(CH) | | | | | | | | | | | | |
| $\omega(NH_2)$ | 90* | (85)* | 87* | (75)* | $\beta$(Si-H) | 80 | (83) | | 80 | (78) | 80 | (78) |
| $\delta$(OCN) | | | | | | | | | | | | |
| $\tau(NH_2)$ | | | 27 | | | | | | | | | |

*) These peaks have contributions from more than one vibrational mode (see text).

Table 2. The vibrational frequencies for liquid $NH_2CHO(ND_2CHO)$ and $NH_2CHO(ND_2CHO)$ in $N_2$ matrix and adsorbed on surfaces.

| Mode | Gas[12,13] | $N_2$ matrix[15] | Liquid[14] | On Ru(001)-2 p(1x2)-0 | On Ni (111)[5] | On Pt(111)[4] | On Si(111)[a] at 220 K |
|---|---|---|---|---|---|---|---|
| $\nu_a(NH)$ | 443 | 440 (330) | 413 (317) | 433 (326) | 415 (313) | 408 (310) | 413 (315) |
| $\nu_s(NH)$ | 427 | 425 (310) | 396 (296) | 400 (295) | 388 (293) | 390 (287) | 398 (305) |
| $\nu(CH)$ | 354 | 356 (358) | 357 (358) | 365 (363) | 355 (357) | 351 (354) | 363 (363) |
| $\nu(CO)$ | 218 | 215 (215) | 210 (207) | 206 (205) | 212 (208) | 209 (205) | 212 (212) |
| $\delta(NH_2)$ | 196 | 197 (135) | 199 (139) | 197 (141) | 199 (139) | 198 (140) | (135) |
| $\delta(CH)$ | 172 | 173 (174) | 172 (173) | 169 (171) | 172 (173) | n.o. (168) | 175* (175) |
| $\nu(CN)$ | 156 | 155 (161) | 162 (166) | | 160 (160) | 160 n.o. | |
| $\rho(NH_2)$ | 143 | 143 (118) | 135 (113) | 138 (114) | -- | n.o. (116) | (110) |
| $\pi(CH)$ | 130 | 128 (128) | 131 (131) | n.o. n.o. | 129 (130) | 132 (133) | 135* (135) |
| $\omega(NH_2)$ | 75 | 81 (60) | 93 (56) | 98 (n.o.) | -- | 85 (66) | (75) |
| $\tau(NH_2)$ | 36 | 50 (27) | 25 (n.o.) | n.o. (n.o.) | -- | n.o. n.o. | 27 (n.o.) |
| $\delta(NCO)$ | 70 | 71 (70) | 75 (71) | 65 (57) | -- | 74 n.o. | 87 (75) |

*) These peaks have contributions from more than one vibrational mode (see text).
a. This work.

Fig. 1a

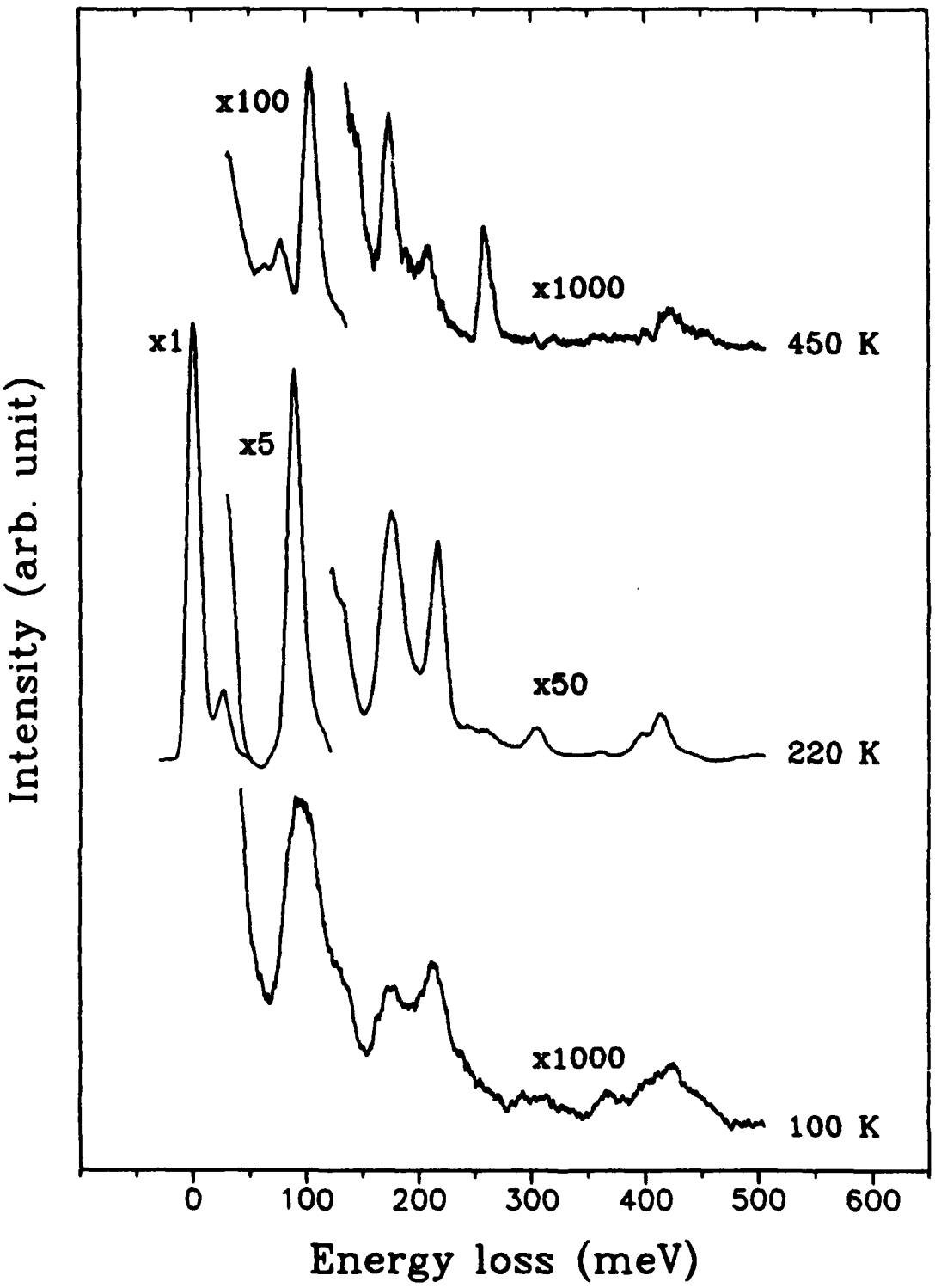

x100
x1000
450 K
x1
x5
x50
220 K
x1000
100 K
Intensity (arb. unit)
0
100
200
300
400
500
600
Energy loss (meV)

Fig. 1b

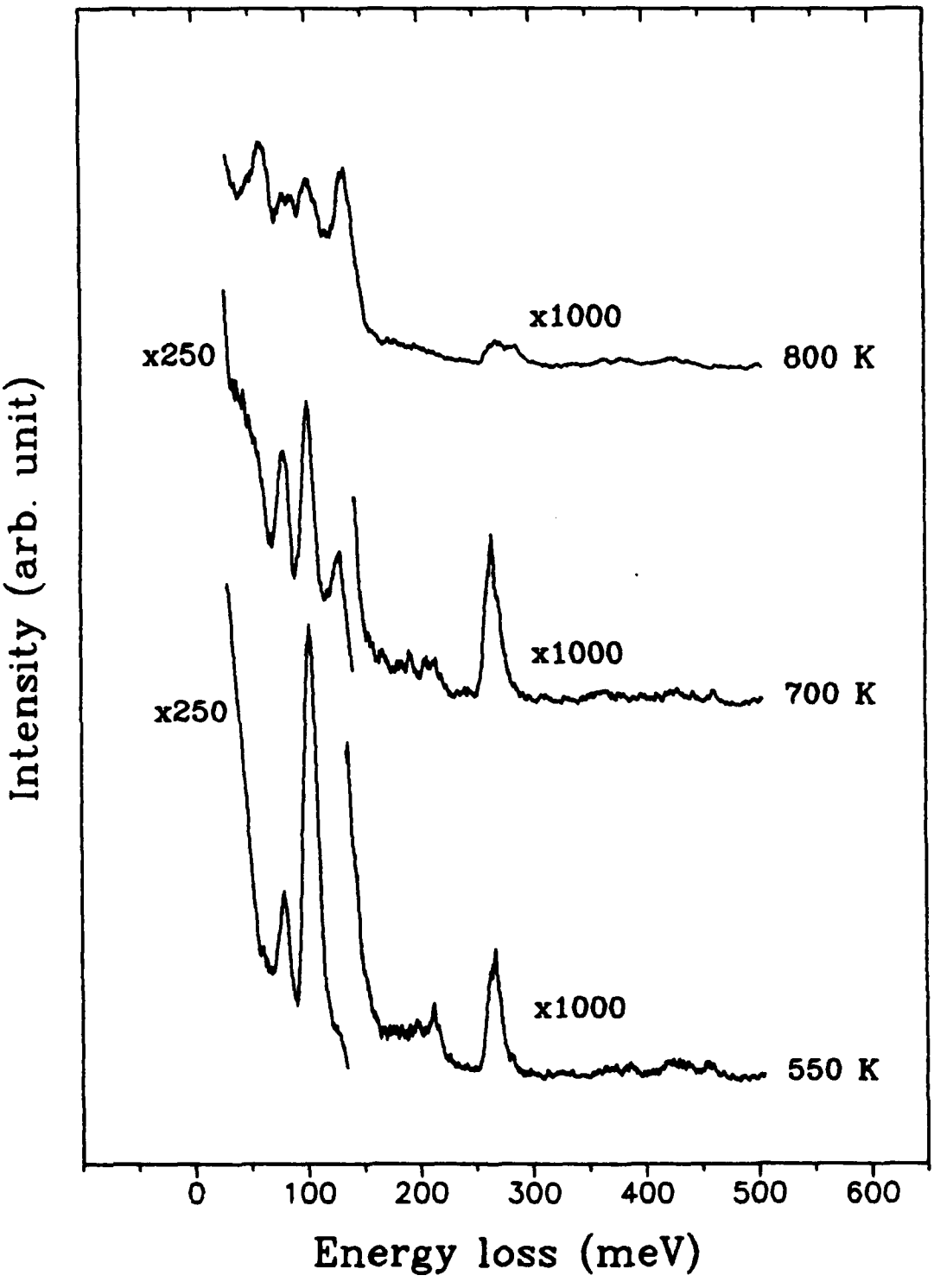

Intensity (arb. unit)
x1000
x250
800 K
x1000
700 K
x250
x1000
550 K
0
100
200
300
400
500
600
Energy loss (meV)

Fig. 2a

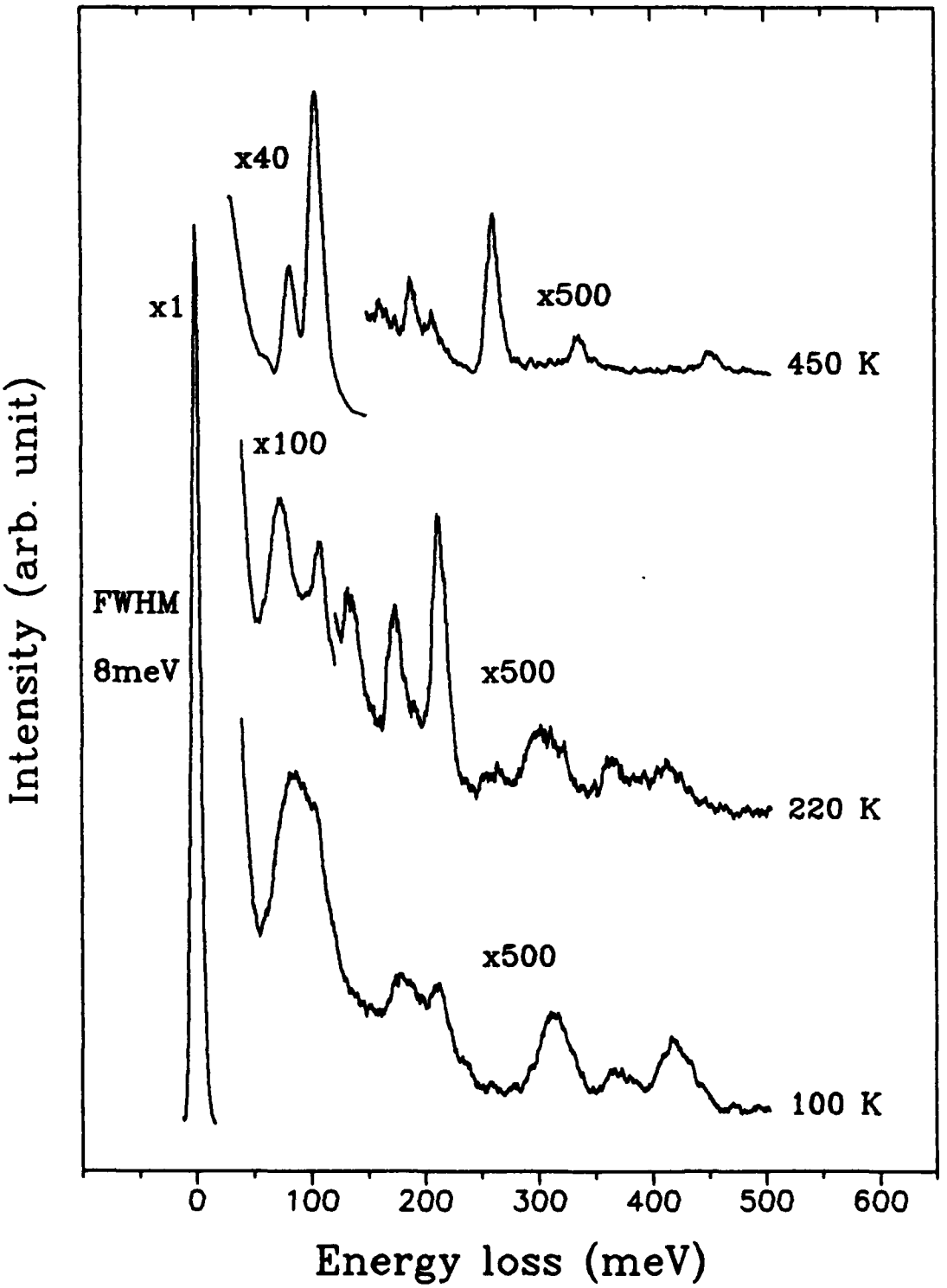

x40
x1
x500
450 K
x100
FWHM
8meV
x500
220 K
x500
100 K
Intensity (arb. unit)
0
100
200
300
400
500
600
Energy loss (meV)

Fig. 2b

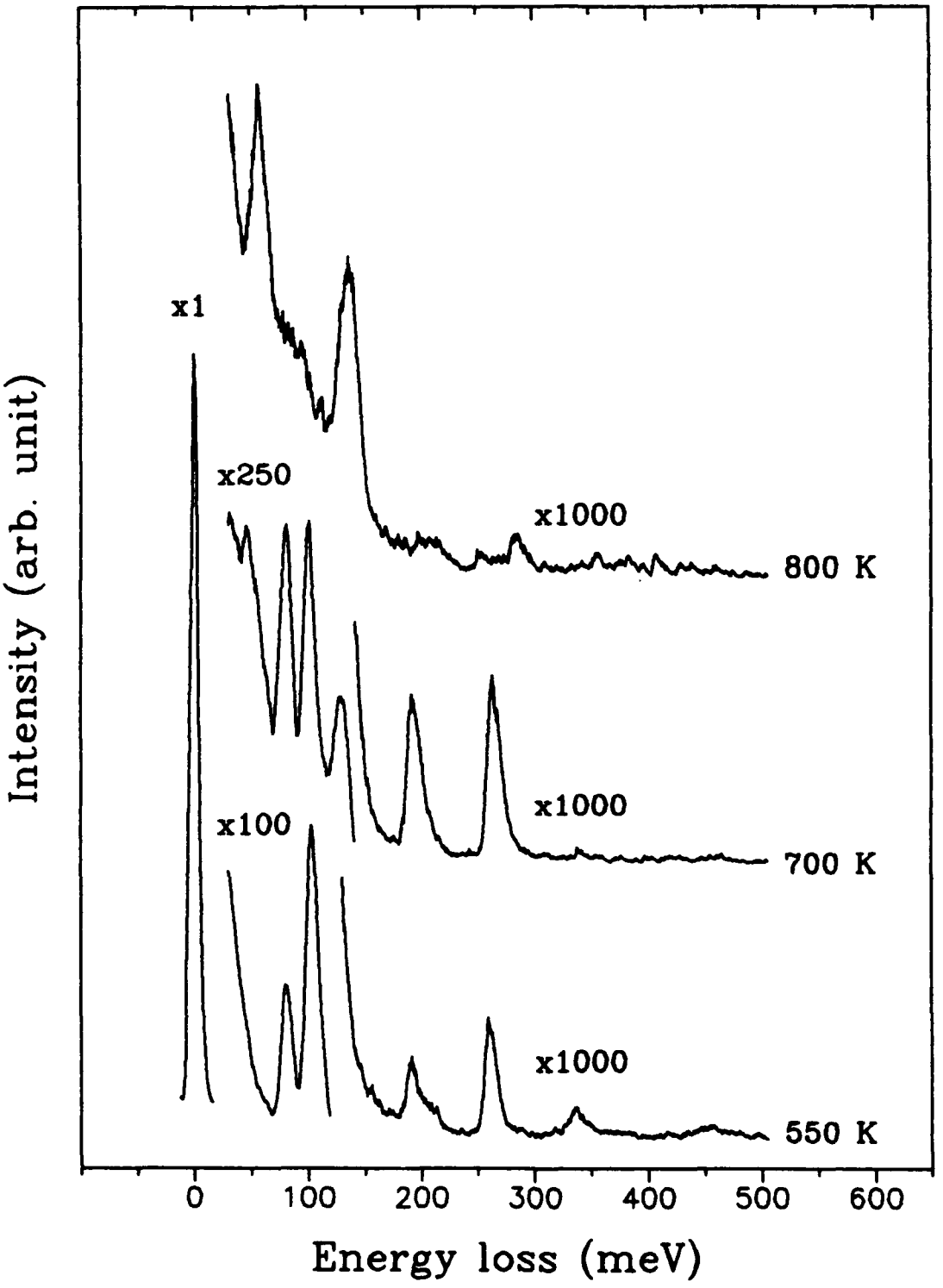

Intensity (arb. unit)
x1
x250
x1000
800 K
x1000
700 K
x100
x1000
550 K
0
100
200
300
400
500
600
Energy loss (meV)

Fig. 3

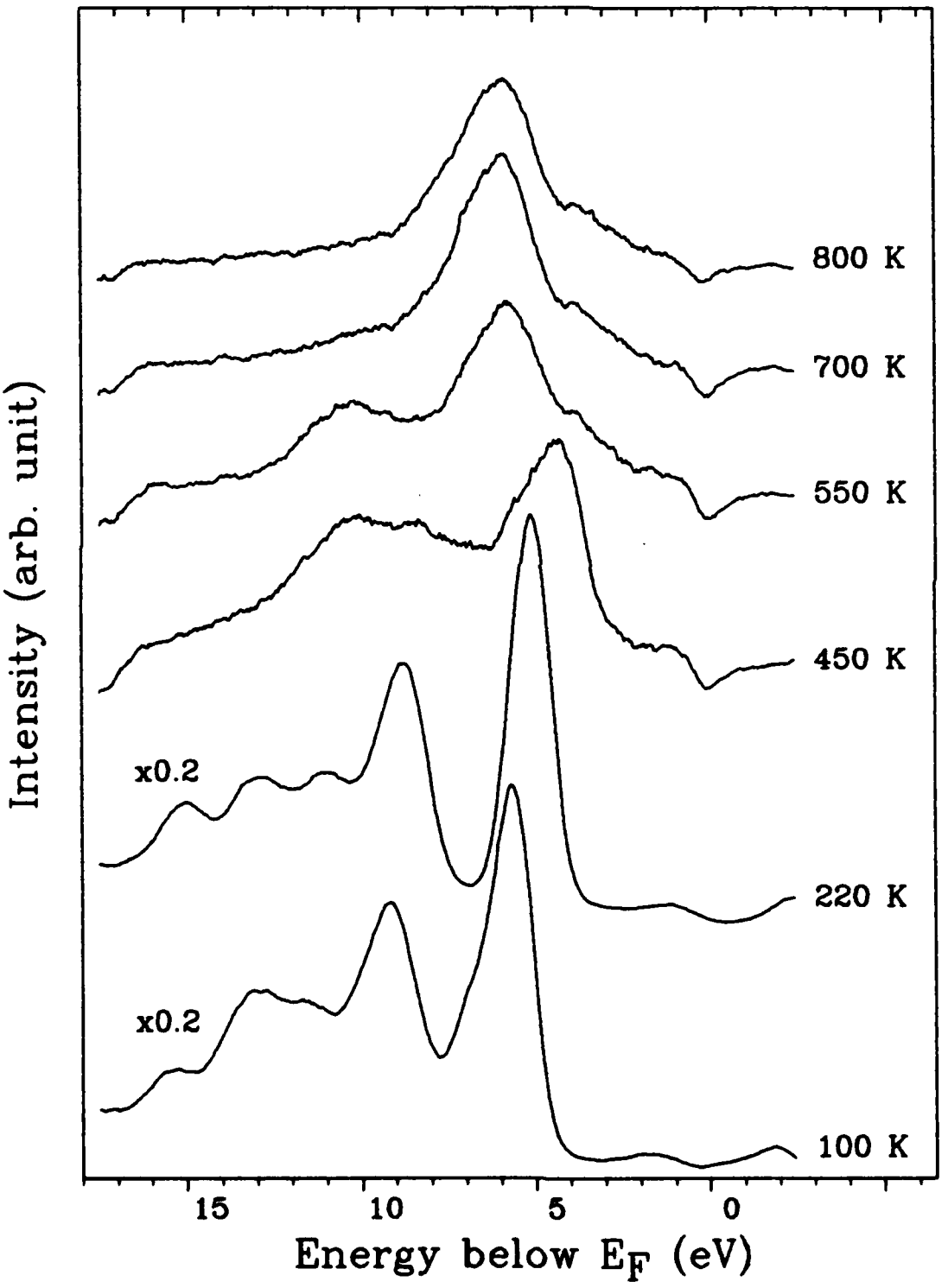
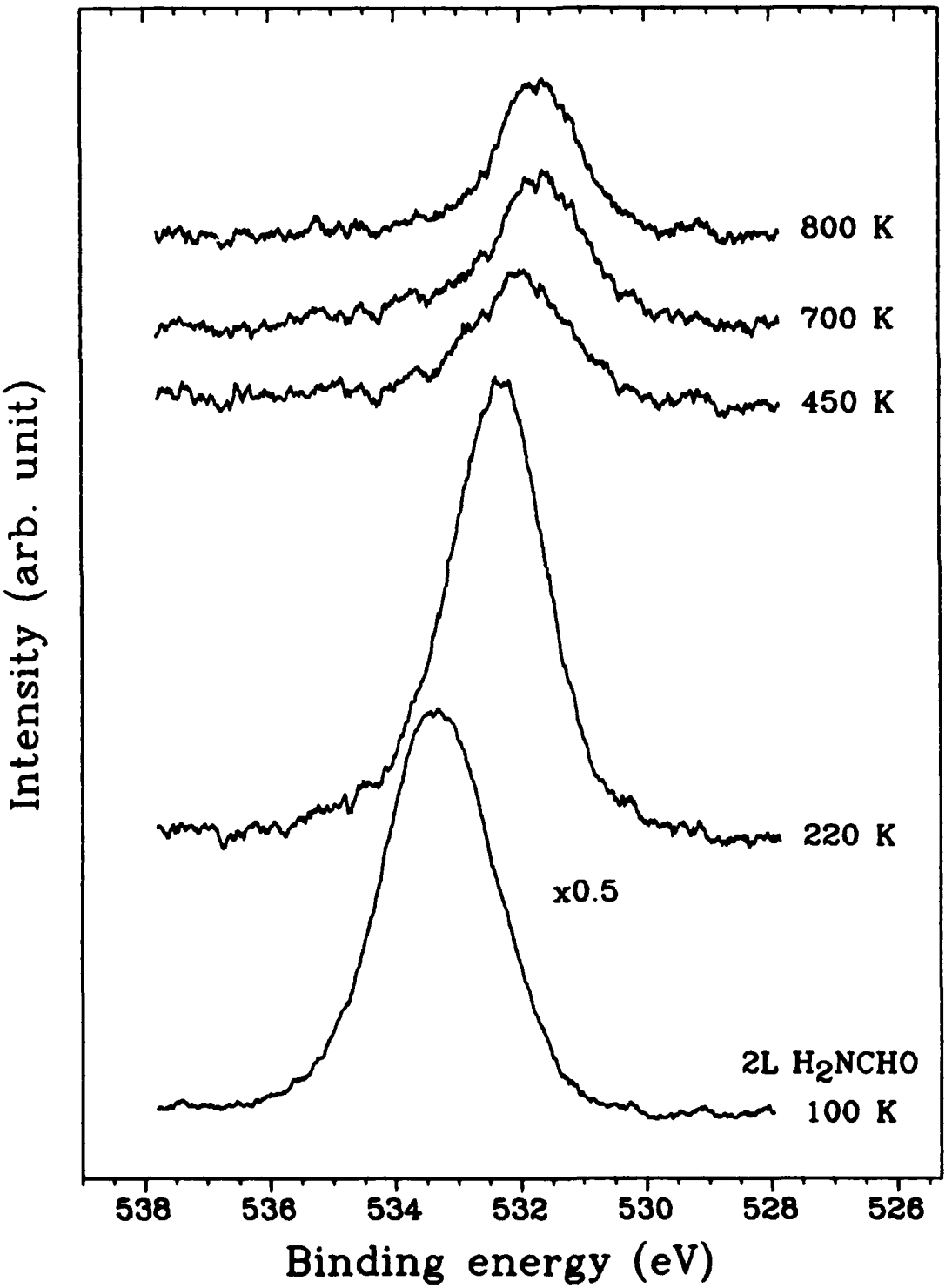

800 K
700 K
550 K
450 K
x0.2
220 K
x0.2
100 K
Intensity (arb. unit)
15
10
5
0
Energy below $E_F$ (eV)

Fig. 4a


800 K
700 K
450 K
220 K
x0.5
2L $H_2NCHO$
100 K
Intensity (arb. unit)
538
536
534
532
530
528
526
Binding energy (eV)

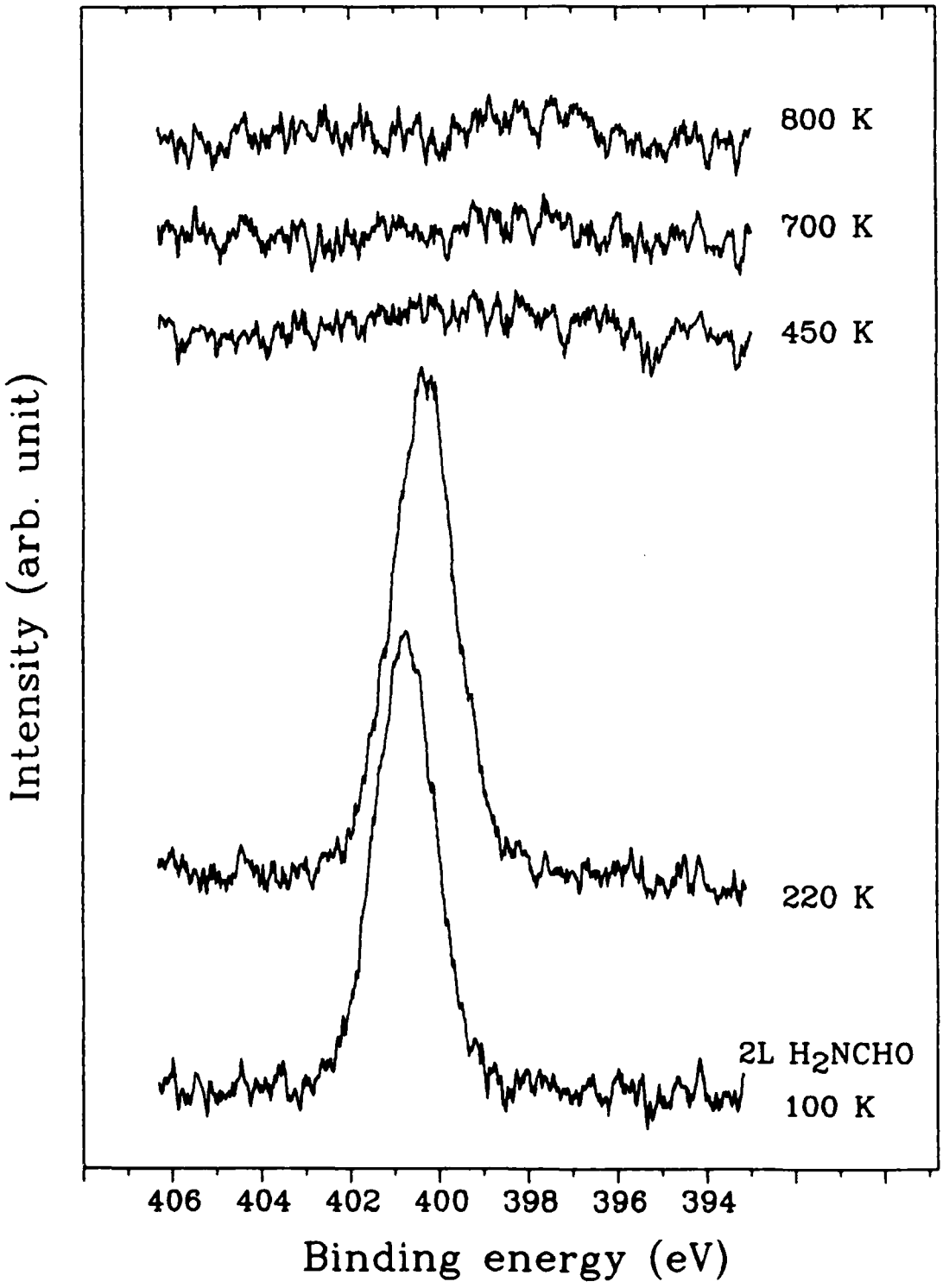
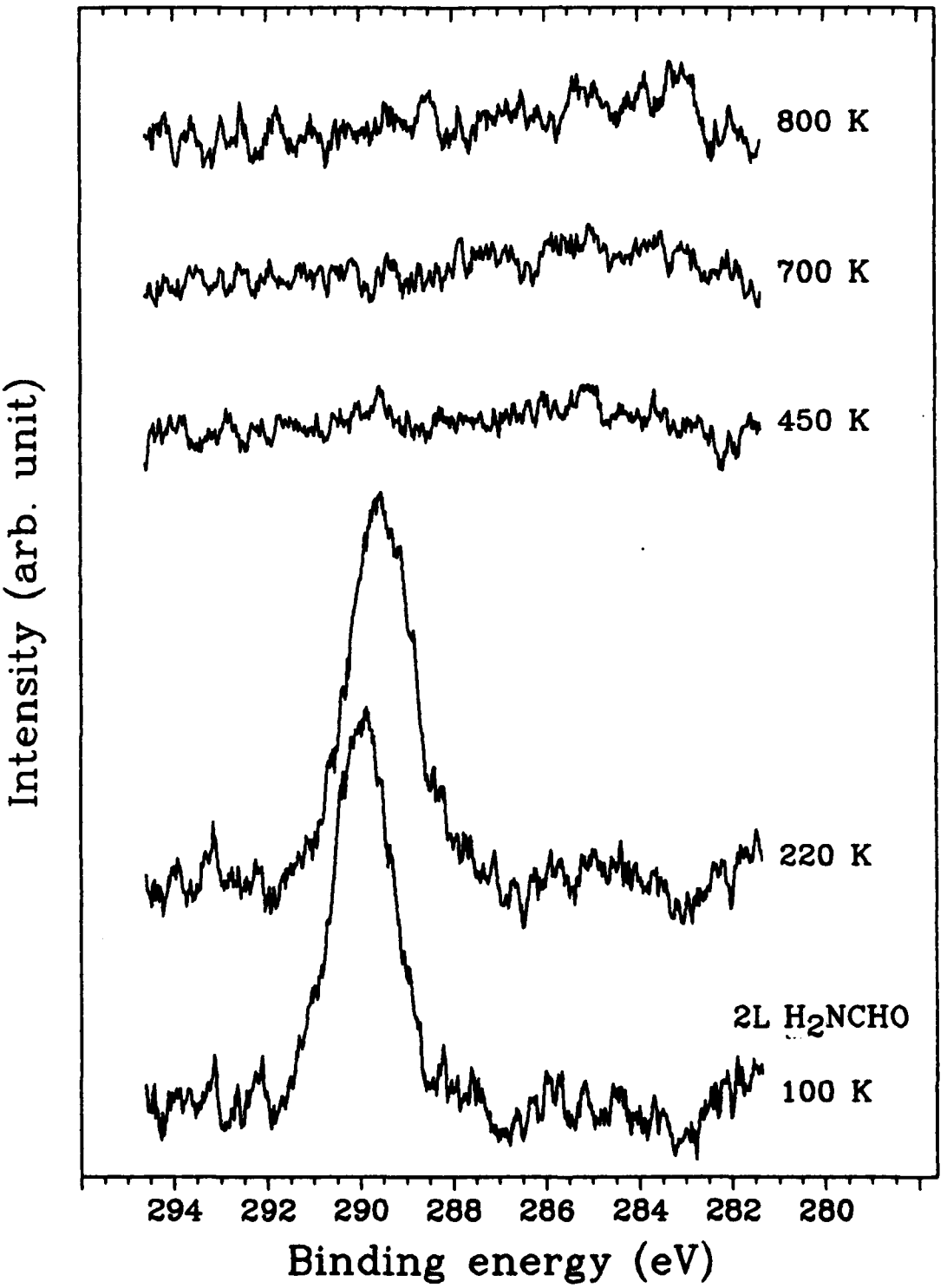

800 K
700 K
450 K
220 K
2L $H_2NCHO$
100 K
Intensity (arb. unit)
406
404
402
400
398
396
394
Binding energy (eV)

Fig. 4c


800 K
700 K
450 K
220 K
2L $H_2NCHO$
100 K
Intensity (arb. unit)
294
292
290
288
286
284
282
280
Binding energy (eV)